ARMY RESEARCH LABORATORY

Colloidal CdTe Nano Crystals Synthesis and Characterization

**by Fred Semendy, Gomatam Jaganathan, Nibir Dhar
Sudhir Trivedi, Ishwara Bhat, and Yuanping Chen**

ARL-TR-4584 **September 2008**

NOTICES

Disclaimers

Army Research Laboratory
Adelphi, MD 20783-1197

ARL-TR-4584 **September 2008**

Colloidal CdTe Nanocrystals Synthesis and Characterization

Fred Semendy, Nibir Dhar, and Yuanping Chen
Sensors and Electron Devices Directorate, ARL

Gomatam Jaganathan and Sudhir Trivedi
Brimrose Corporation

Ishwara Bhat
ECSE Department, Renssalear Polytechnic Institute

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* September 2008	**2. REPORT TYPE** Final	**3. DATES COVERED (From - To)** 2007 to 2008
4. TITLE AND SUBTITLE Colloidal CdTe Nano Crystals Synthesis and Characterization		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Fred Semendy, Gomatam Jaganathan, Nibir Dhar, Sudhir Trivedi, Ishwara Bhat, and Yuanping Chen		**5d. PROJECT NUMBER**
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-SE-EI 2800 Powder Mill Road Adelphi, MD 20783-1128		**8. PERFORMING ORGANIZATION REPORT NUMBER** ARL-TR-4584
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		**10. SPONSOR/MONITOR'S ACRONYM(S)**
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Synthesis of CdTe nano crystals (NCs) in uniform sizes and in good quality was performed in our nano lab and further characterized by absorption spectra, photoluminescence (PL), and atomic force microscopy (AFM). In this growth procedure, CdTe nano crystal band gap is strongly dependent on the growth time and not on the injection temperature or organic ligand concentration. This is very attractive because the nano crystal size can be easily controlled by the growth time only and is very attractive for large scale synthesis. The color of the solution changes from greenish yellow to light orange, then to deep orange and finally grayish black to black over a period of one hour. This is a clear indication of the gradual growth of different size (and different band gap) of CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap can be controlled by adjusting the growth time after injection of the tellurium. The prepared CdTe NCs were characterized by absorption spectra, photoluminescence (PL), AFM and X-ray diffraction. Measured absorption maxima are at 521, 560, 600, and 603 nm corresponding to band gaps of 2.38, 2.21, and 2,07 eV respectively for growth times of 15, 30, 45, and 60 minutes. From the absorption data, nano crystal growth size saturates out after 45 minutes. AFM scanning of these materials indicate that the size of these particles is between 4 to 10 nm in diameter for the growth time of 45 minutes. This report presents growth and characterization data on CdTe nano crystals for various growth times.

15. SUBJECT TERMS

Nano crystals, CdTe, Luminescence, AFM, Bandgap

16. Security Classification of:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Fred Semendy
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** (*Include area code*)
U	U	U	SAR	16	301-394-4627

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures iv

1. Introduction 1

2. Experimental 1

3. Results and Discussion 2

4. Conclusions 7

5. References 8

Distribution List 9

List of Figures

Figure 1. CdTe nano crystal growth solution as a function of growth time of 15 min, 30 min, 45 min, and 60 min. 2

Figure 2. Absorption spectrum of CdTe nano crystals grown at different times. 3

Figure 3. Luminescence spectrum of CdTe nano crystals after 30 and 45 minutes 4

Figure 4. AFM picture of CdTe nano crystals drop cast on 211 Silicon 5

Figure 5. Localized depth picture of CdTe nano crystals drop casted on 211 Silicon. 5

Figure 6. 3d CdTe nano crystals by AFM. 6

Figure 7. Step height measurement of nano particles. 6

1. Introduction

II-VI type of nano Crystal are extensively studied for their optoelectronic, photochemical, and nonlinear optical properties (*1, 2, 3*). Semiconductor nano crystals, like CdTe, show size dependent optical properties and are very important in basic nano science research, colloidal science, biomedical labeling, light emitting diodes, solar cells, and lasers (*4-6)*. In general, semiconductor nano crystals show novel optical and electronic properties when they have size comparable to, or smaller than, the dimensions of the exciton within their corresponding bulk material. This allows us to create unique properties for the nano crystal by engineering the size and composition and the chemical functionality of their surrounding medium. The techniques and capability of this manipulation of the size is an important way to create desired nano crystals (*7, 8*). By using size-selective precipitation techniques, cadmium chalcogenide NCs have been successfully obtained (*9*). The most common semiconductor materials grown by precipitation technique are CdTe, CdSe, CdS, and ZnS of which CdTe has special technological importance because it is the only known II-VI material that can form conventional p-n junctions (*10*). There are many reports on the synthesis of semiconductor nano crystals with very good monodispercity (*11-13*). Synthesis involving injection method give NCs with good quality. Usually injection is carried out at a certain temperature. Nano crystal preparation can also be done with non injection synthesis without nucleation initiators (*14*). The formation of high-quality nano crystal is often favored.

2. Experimental

Colloidal CdTe nano crystals were synthesized using the method of Cao (*14*) and Lifshitz (*15*). The synthesis was carried out as follows. A highly purified tellurium (Te) solution was prepared in tri octylphosphine (TOP) and octadecene (ODE). In an experiment 0.128 gm of Te and 0.2112 gm of TOP was added to ODE so that total was 2 mL. The cadmium (Cd) precursor solution was prepared by mixing cadmium oxide (CdO) and an oleic acid (OA) and ODE mixture. In the experiment 0.0256 gm of CdO and 200 µL of OA and 10 mL of ODE were used. CdO was dissolved in OA/ODE mixture when heated under Ar flow at 240 ºC. A grey precipitate was formed when further heated to 270 ºC which was characterized as Cd particles and considered as the first stage of the reaction. The second part of the reaction included an instantaneous injection of the Te precursor which was previously prepared to the Cd solution at 270 ºC solution. Immediate reaction takes place and CdTe nano crystals formed. Immediately after the injection, the color of the solution started changing from greenish yellow to light orange and then to deep orange and finally grayish black over a period of one hour. Aliquots of the CdTe nano crystals were withdrawn 15, 30, 45, and 60 minutes after injection and dispersed in toluene. The

dispersed mixture was centrifuged at 3000 rpm for 5 minutes. The supernatant liquid – CdTe nano crystals dispersed in toluene was separated and characterized for absorption, photoluminescence, substrate surface and particle size determination using AFM.

3. Results and Discussion

CdTe nano crystal solutions in toluene for reaction times of 15, 30, 45, and 60 min shown in figure 1, were used to obtain the absorption spectra using a Perkin Elmer UV-visible Lambda 19 spectrometer. All luminescence measurements were acquired by using a Renishaw *inVia* Reflex confocal Raman microscope (Hoffman Estates, Illinois) equipped with three independent excitation sources (514, 633, and 785 nm). The 514 nm was focused onto the sample at the microscope stage through either a 50 (N.A. 0.75) or 100 (N.A. 0.90) objective. Before all measurements, the instrument was wavelength calibrated by using an internal Si standard. Each spectrum was collected and stored. AFM scanning of the nano crystals on silicon was done with Digital Instruments (DI) tapping mode technique.

The color of the nano crystal growth solution as a function of time after the initial injection is presented in figure 1. The picture shows the four different solutions obtained after various injection times as indicated. One can clearly see the change in color indicative of the difference in the size of particles from left to right. In our case, the size difference was the primary concern.

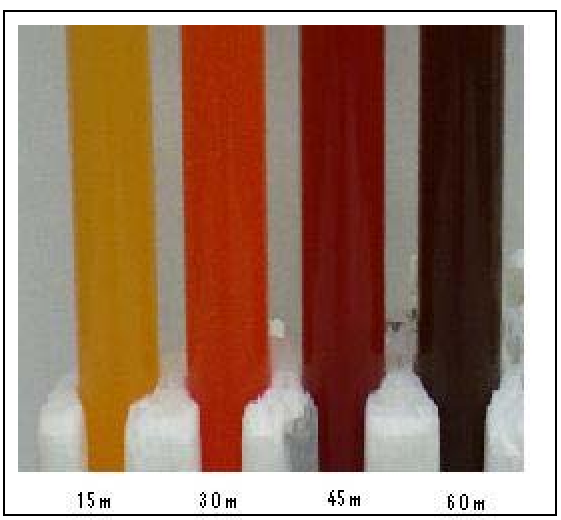

Figure 1. CdTe nano crystal growth solution as a function of growth time of 15 min, 30 min, 45 min, and 60 min.

Immediately after injection, the color of the solution started changing from greenish yellow to light orange then to deep orange and finally grayish black to black over a period of one hour. This is a clear indication of the gradual growth of different size (and different band gap) CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap can be controlled, by adjusting the growth time after injection of the tellurium. The grayish black and black solutions are not included in the picture. As the time changed, the particle size changed and correspondingly the band gap also changed. The size change continued for an hour where it reached the saturation point.

Figure 2 shows the absorption spectra of the nano crystals grown at various times. As can be seen, there is a shift of absorption peak as well as the band gap as the time of growth changes. Clearly the sixty minute growth sample indicates the saturation in terms of the peak position as well as the band gap. The absorption maxima are at 521, 560, 600, and 603 nm respectively corresponding to band gaps of 2.38, 2.21, and 2.07. It appears that nano crystal growth size saturates out between 45 and 60 minutes indicating no further shift in the peak height nor band gap change.

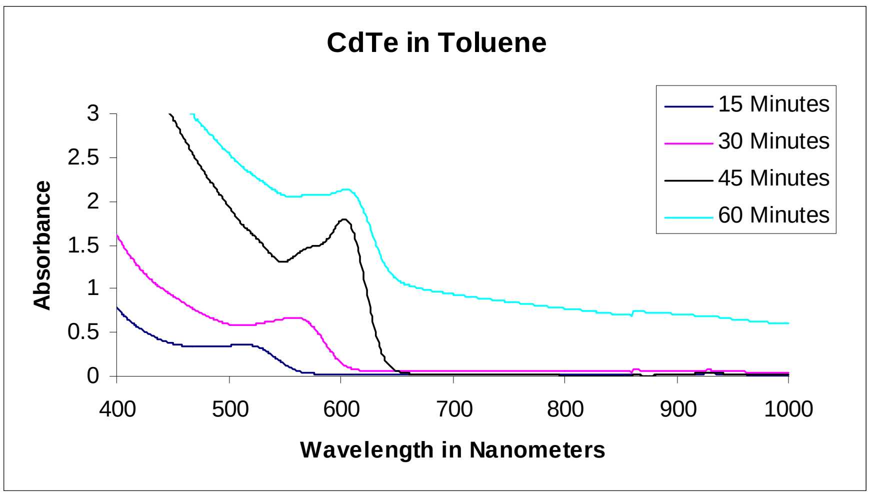

Figure 2. Absorption spectrum of CdTe nano crystals grown at different times.

The luminescence spectrum of the CdTe nano crystals synthesized 30 minutes and 45 minutes after injection of the tellurium precursor are presented in figure 3.

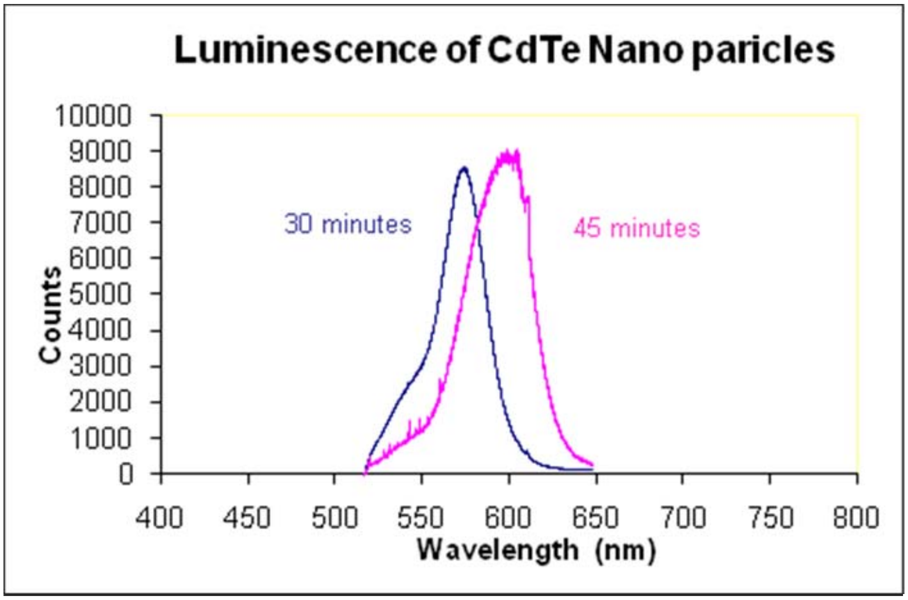

Figure 3. Luminescence spectrum of CdTe nano crystals after 30 and 45 minutes

In the case of the luminescence, the FWHM increases from 27 nm for the 30 minute growth sample and to 32 nm for the 45 minute growth sample. Red shifting of luminescence with respect to temperature change has been reported before for the temperature dependent growth of CdTe nano particles (*16*). In this procedure, as shown by the results, high quality CdTe nano crystal growth was based upon time and not on the injection temperature or the organic ligand concentration; also shown is the red shift of the luminescence. Since this is similar to the previous results, the time dependent growth also becomes an attractive way of growth for the large-scale synthesis of nano crystals.

Surface morphology of CdTe nano crystals was determined by atomic force microscopy. Sample preparation with drop casting always resulted in piling up of the nano crystals and did not result in uniform thin film. This is usually the case with drop casting and to avoid piling up and to obtain uniform film spin casting method needed to be adopted. We tried extensively to produce close packed continuous nano crystalline thin film. Spin casting was tried using several dilutions of nano crystals in chloroform with different rotation speeds and time. In many cases we ended up with islands of mono layer of nano crystalline film with spots of 3-D aggregates over the entire substrate surface. This type of deposition occurs always when nano crystalline film is deposited on solid substrate surfaces like silicon (*17*). But for our AFM study both drop casted and spun samples were used. CdTe nano crystalline film was formed on Si[211] substrate either by spin casting or drop casting. In a special case, the nano crystals grown at 45 minutes were initially drop casted on 211 silicon substrate and studied by Atomic Force Microscopy (AFM) and the AFM pictures are presented in figure 4. As can be seen, the AFM image the particle

height is 4.2 nm and the particles are distributed unevenly. The following is the bearing chart which characterizes the relative roughness of the surface in terms of high and low areas.

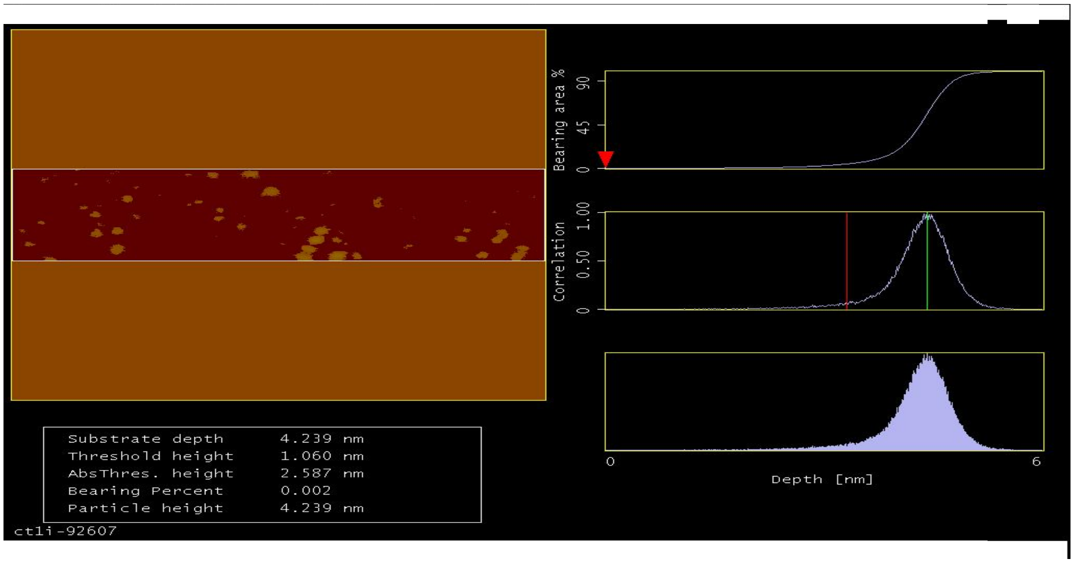

Figure 4. AFM picture of CdTe nano crystals drop cast on 211 Silicon .

Figure 5 gives the localized depth data within a specified area and it shows that a particular dot was chosen for the analysis and the chosen box indicates that the size of the nano particle is about 4.7 nm.

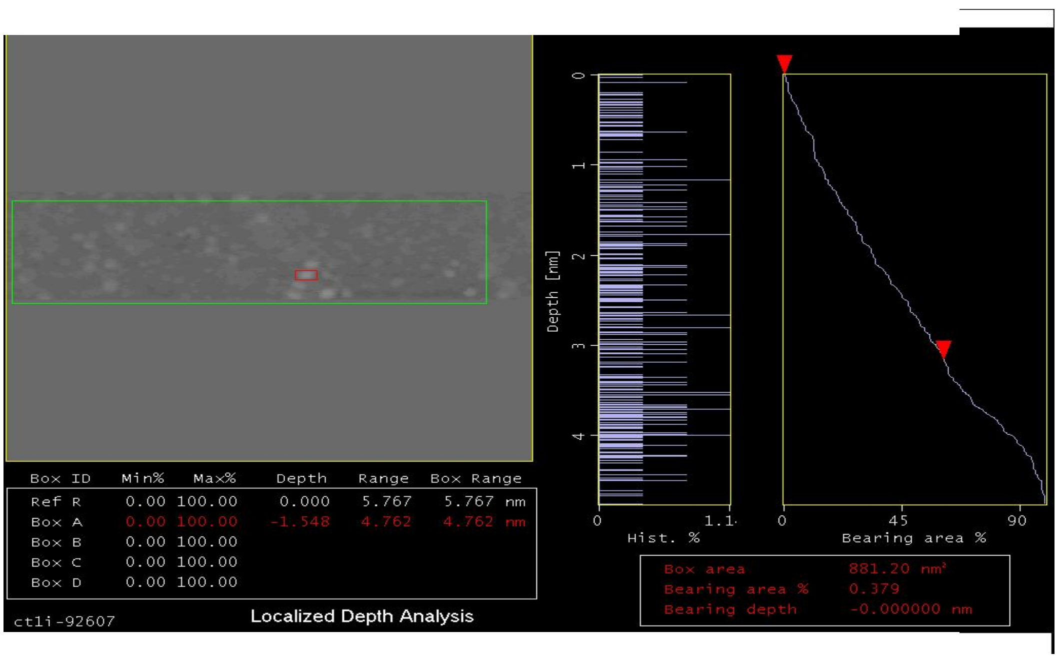

Figure 5. Localized depth picture of CdTe nano crystals drop casted on 211 Silicon.

Figure 6 she 3d version of the roughness plot of the nano crystals. One can see that the particles are randomly scattered and in general of uniform size. Figure 7 gives the top view image with the reference lines drawn across the region to be measured. The height profile is generated from averaged data in the referenced region. The midlevel horizontal line to the top gives a height of 80 nm and clearly the height of these particles are below 10 nm.

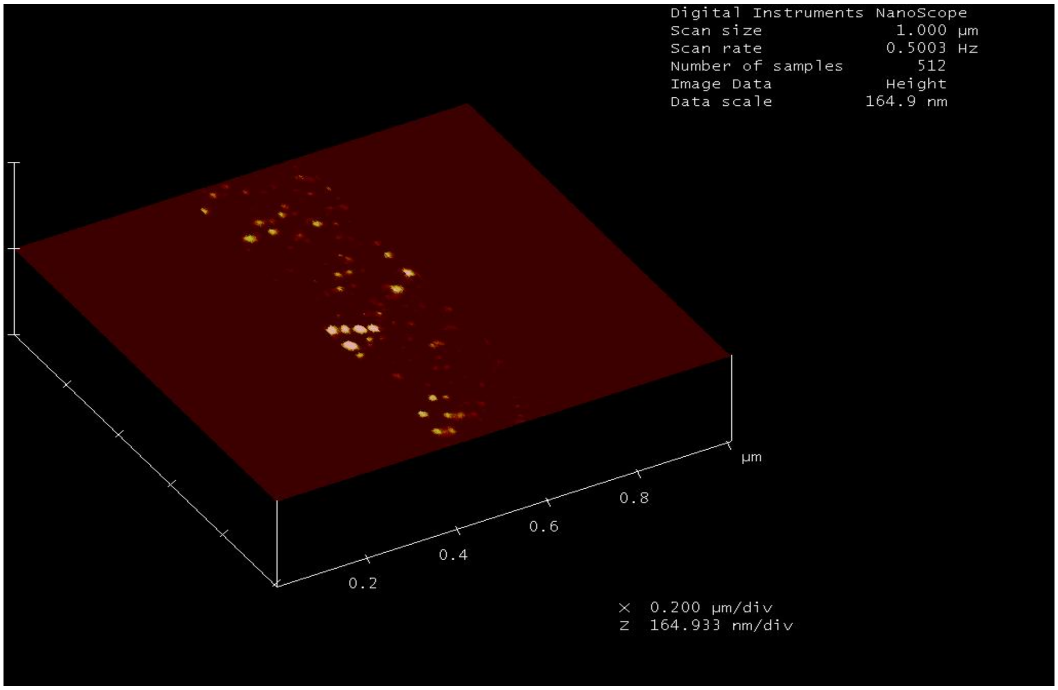

Figure 6. 3d CdTe nano crystals by AFM.

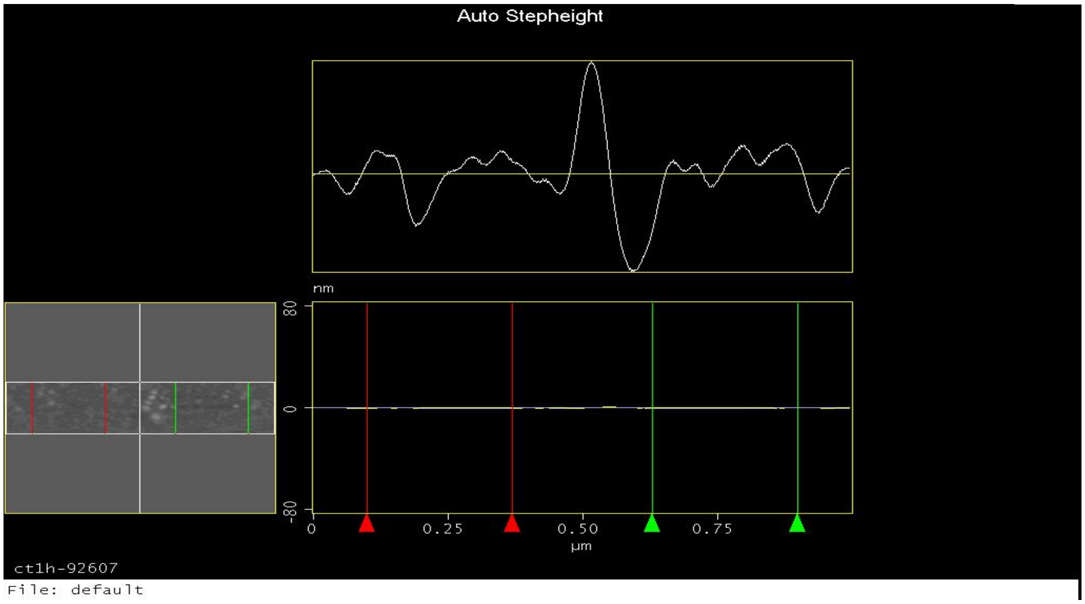

Figure 7. Step height measurement of nano particles.

4. Conclusions

In this work we have modified the synthesis procedure of CdTe nano crystals from temperature, or ligand concentration based growth to time dependent growth. In this synthesis procedure, CdTe nano crystal band gap is strongly dependent on the growth time and not on the injection temperature or organic ligand concentration. We think that this procedure is very attractive because that the size of nano crystal can be easily controlled by the growth time only and hence useful for large scale synthesis. A growth based upon time will more likely provide uniform nano particles compared to a growth based on temperature, since uniform temperature is difficult to obtain in a reaction flask. The color of the solution changed from greenish yellow to light orange then to deep orange and finally grayish black to black over a period of one hour. This was a clear indication of the gradual growth of different size (and different band gap) of CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap could be controlled by adjusting the growth time after injection of the tellurium. Results of absorption spectra, photoluminescence (PL), and AFM were presented. Measured absorption maxima were found to be at 521, 560, 600, and 603 nm corresponding to band gaps of 2.38, 2.21, and 2.07 eV respectively for growth times of 15, 30, 45 and 60 minutes. From the absorption data one can see that nano crystal growth size saturates out after 45 minutes. AFM scanning of these materials indicate that the size of these particles are about 3-10 nm in radius for growth time of 45 minutes.

5. References

1. Bawandi, M.; Steigerwald, M.; Brus, I. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
2. Alivisatos, P. *Science 271* **1996**, 933.
3. Markovich, G.; Collier, C.; Henrichs, S.; Remacle, F.; Levine, R.; Heath, J. *Acc. Chemm. Res.* **1999**, *32*, 415.
4. Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Martoussi, H. *Nature Mater.* **2005**, *4*, 435.
5. Peng, A.; Peng, X. G. *J. Am.Chem. Soc.* **2002**, *124*, 3343.
6. Peng, X. G.; Manna, L.; Yang, W. D.; Wickam, J.; Scher, E.; Kadanvich, A.; Alvisatos, A. P. *Nature* **2000**, *404*, 59.
7. Coe, S.; Woo, W.; Bawendi, M.; Bulovic, V. *Nature* **2000**, *404*, 59.
8. Lieber, C. *Solid State Commmun* **1998**, *107*, 607.
9. Murray, C.; Norris, D.; Bawendi, M. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
10. McCaldin, J. *J. Vac. Sci. Technol* **1990**, *A*, *8*, 1188.
11. Cumberland, S. L.; Hanif, K. M.; Javier, A.; Khitrov, G. A.; Strouse, G. F.; Woessner, S. M.; Yun, C. *Chem. Mater* **2002**, *14*, 1576.
12. Pradhan, N.; Efrima, S. *J. Am.Chem. Soc.* **2003**, *125*, 2050.
13. Talapin, D. V.; Haubold, S.; Rogach, A. L.; Kornowski, A.; Hasse, M.; Weller, H. *J. Phys. Chem,B.* **2001**, *105*, 2260.
14. Yang, Y. A.; Wu, H.; Williams, K. R.; Chao, Y. C. *Angew. Chem. Int. Ed* **2005**, *44*, 6712.
15. Kolney-Olesiak, J.; Kloper, V.; Osovsky, R.; Sashchiuk, A.; Lifshitz, E. *Surf. Sci* **2007**, *601*, 2667.
16. Walker, G. W.; Sunder, V. C.; Rudzinski, C. M.; Wun, A. W.; Baeendi, M. G.; Nocera, D. G. *App. Phys. Lett*. **2003**, *83*, 3555.
17. Mott, L.; Billoudet, F.; Lacaze, E.; Douin, J.; Pileni, M. P. *J. Phys. Chem, B* **1997**, *101*, 138.

No. of Copies	Organization
1 (ELECT COPY)	ADMNSTR DEFNS TECHL INFO CTR ATTN DTIC OCP 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DARPA ATTN IXO S WELBY 3701 N FAIRFAX DR ARLINGTON VA 22203-1714
1 CD	OFC OF THE SECY OF DEFNS ATTN ODDRE (R&AT) THE PENTAGON WASHINGTON DC 20301-3080
1	US ARMY RSRCH DEV AND ENGRG CMND ARMAMENT RSRCH DEV AND ENGRG CTR ARMAMENT ENGRG AND TECHNLGY CTR ATTN AMSRD AAR AEF T J MATTS BLDG 305 ABERDEEN PROVING GROUND MD 21005-5001
1	US ARMY TRADOC BATTLE LAB INTEGRATION & TECHL DIRCTRT ATTN ATCD B 10 WHISTLER LANE FT MONROE VA 23651-5850
1	US ARMY INFO SYS ENGRG CMND ATTN AMSEL IE TD F JENIA FT HUACHUCA AZ 85613-5300
1	COMMANDER US ARMY RDECOM ATTN AMSRD AMR W C MCCORKLE 5400 FOWLER RD REDSTONE ARSENAL AL 35898-5000
1	US GOVERNMENT PRINT OFF DEPOSITORY RECEIVING SECTION ATTN MAIL STOP IDAD J TATE 732 NORTH CAPITOL ST NW WASHINGTON DC 20402

No. of Copies	Organization
5	ECSE DEPARTMENT RENSSALEAR POLYTECHNIC INSTITUTE ATTN I BHAT TROY NJ 12180
10	BRIMROSE CORP OF AMERICA ATTN G JAGANATHAN (5 COPIES) ATTN S TRIVEDI (5 COPIES) 19 LOVERTON LN SPARKS MD 21152
1	US ARMY RSRCH LAB ATTN AMSRD ARL CI OK TP TECHL LIB T LANDFRIED BLDG 4600 ABERDEEN PROVING GROUND MD 21005-5066
1	DIRECTOR US ARMY RSRCH LAB ATTN AMSRD ARL RO EV W D BACH PO BOX 12211 RESEARCH TRIANGLE PARK NC 27709
66	ARMY RSRCH LAB ATTN AMSRD ARL SE EE T ALEXANDER ATTN AMSRD ARL CI OK PE TECHL PUB ATTN AMSRD ARL CI OK TL TECHL LIB ATTN AMSRD ARL SE DE M LITZ ATTN AMSRD ARL SE E G WOOD ATTN AMSRD ARL SE EE K ALIBERTI ATTN AMSRD ARL SE EE N GUPTA ATTN AMSRD ARL SE EE R TOBER ATTN AMSRD ARL SE EI J LITTLE ATTN AMSRD ARL SE EI K OLVER ATTN AMSRD ARL SE EI P FOLKES ATTN AMSRD ARL SE EI S SVENSSON ATTN AMSRD ARL SE EM M WRABACK ATTN AMSRD ARL SE R P AMIRTHARAJ ATTN AMSRD ARL SE RE C FAZI ATTN AMSRD ARL SE RL M DUBEY

No. of Copies | Organization

ATTN AMSRD-ARL-SE-DE
K BLAINE
ATTN AMSRD-ARL-SE-DP A LELIS
ATTN AMSRD-ARL-SE-DP
B MORGAN
ATTN AMSRD-ARL-SE-E
H POLLEHN
ATTN AMSRD-ARL-SE-E L BLISS
ATTN AMSRD-ARL-SE-E T BOWER
ATTN AMSRD-ARL-SE-E0 N FELL
ATTN AMSRD-ARL-SE-EE B ZANDI
ATTN AMSRD-ARL-SE-EI
D BEEKMAN
ATTN AMSRD-ARL-SE-EI G BRILL
ATTN AMSRD-ARL-SE-EI
J GOMATHAM
ATTN AMSRD-ARL-SE-EI K K CHOI
ATTN AMSRD-ARL-SE-EI N DHAR
(5 COPIES)
ATTN AMSRD-ARL-SE-EI
P TAYLOR
ATTN AMSRD-ARL-SE-EI
P WIJEWAMASURIYA
ATTN AMSRD-ARL-SE-EI W BECK
ATTN AMSRD-ARL-SE-EI
W SARNEY
ATTN AMSRD-ARL-SE-EI Y CHEN
(5 COPIES)
ATTN AMSRD-ARL-SE-EM
F SEMENDY (5 COPIES)
ATTN AMSRD-ARL-SE-EM G DANG
ATTN AMSRD-ARL-SE-EM
G GARRETT
ATTN AMSRD-ARL-SE-EM
G SIMONIS
ATTN AMSRD-ARL-SE-EM M REED
ATTN AMSRD-ARL-SE-EM
M TAYSING-LARA
ATTN AMSRD-ARL-SE-EM
N BAMBHA
ATTN AMSRD-ARL-SE-EM N DAS
ATTN AMSRD-ARL-SE-EM P SHEN
ATTN AMSRD-ARL-SE-EM
W CHANG
ATTN AMSRD-ARL-SE-RE
A DARWISH
ATTN AMSRD-ARL-SE-RL
A WICKENDEN
ATTN AMSRD-ARL-SE-RL
D EWING
ATTN AMSRD-ARL-SE-RL
E ZAKAR
ATTN AMSRD-ARL-SE-RL
J COSTANZA
ATTN AMSRD-ARL-SE-RL K JONES
ATTN AMSRD-ARL-SE-RL
M DERANGE
ATTN AMSRD-ARL-SE-RL P SHAH
ATTN AMSRD-ARL-SE-RL
S KILPATRICK
ATTN IMNE ALC IMS MAIL &
RECORDS MGMT
ADELPHI MD 20783-1197

Total: 91 (89 HC, 1 CD, 1 ELECT)